Competing interactions in multiferroics and low-dimensional systems
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Chapter 1

Introduction

In recent years a wide variety of experimental observations and theoretical results have shown that many transition metal oxides exhibit a broad range of interesting phenomena, including colossal magnetoresistance where enormous changes in resistance are produced by small variations of a magnetic field, and high temperature superconductivity that exists in layered copper oxides. An important feature of these materials is the existence of several competing tendencies, manifested in their rich phase diagrams and nonlinear responses. This electronic complexity found in transition metal oxides is also of potential interest for long-term technological applications because it makes possible to make use not of charge (usual semiconductor electronics) or charge and spin (spintronics) but also of orbital and lattice degrees of freedom. The competition and cooperation between these degrees of freedom typically lead to giant responses to small external stimuli, such as magnetic field, electric field and mechanical stress.

This thesis deals with different aspects of systems with competing interactions. In particular, we focus on materials called multiferroics that display cross-correlations between magnetic and electronic properties. Additionally, we study quasi-one-dimensional materials where the electron-lattice coupling (or spin-lattice coupling) plays a dominant role resulting in a transition into a state with periodic modulation of the charge (spin) density at sufficiently low temperatures.

Whereas a ferroelectric crystal possesses a spontaneous polarization that can be reversed or reoriented by applying an electric field, a ferromagnet exhibits a spontaneous and switchable magnetization. Multiferroic materials that exhibit both of these properties have been attracting enormous interest recently for fundamental reasons and for possible applications. The latter results from the technological desire to control magnetic properties by electric
fields. Multiferroicity is closely related to the linear magnetoelectric effect which consists in the induction of magnetization by means of an electric field and, vice versa the induction of polarization by means of a magnetic field.

Despite the different origins of ferroelectricity and magnetism in solids — ferromagnetism arises through the quantum mechanical phenomenon of exchange, while electric polarization is manifested in the form of cooperative atomic displacements — a number of interesting parallels exist between these phenomena. For example, similarities in the thermodynamics of ferroelectrics and ferromagnets such as their behavior in external fields, anomalies that occur at a critical temperature, and the properties of domain structures result from the analogy between the equations of magnetostatics and electrostatics in polarizable media.

The possibility of an intrinsic correlation between magnetic and electric properties was discussed at an early stage by Pierre Curie in 1894: “Les conditions de symétrie nous permettons d’imaginer qu’un corps à molécule dissymétrique se polarise peut-être magnétiquement lorsqu’on le place dans un champ électrique.”[1] Historically, the first observation of such a phenomenon is the so-called linear magnetoelectric effect found in chromium oxide (Cr$_2$O$_3$) by Astrov in 1960.[2] Since any dielectric quantity is symmetric and any magnetic quantity is antisymmetric under time reversal symmetry ($T$), the linear magnetoelectric effect only occurs in systems that break time reversal symmetry, for example, by a magnetic ordering. The search for multiferroics was very active in the 1960s and 1970s and several compounds have been found such as BiMnO$_3$, BiFeO$_3$, YMnO$_3$, Pb(Fe$_{2/3}$,W$_{1/3}$)O$_3$, Pb(Fe$_{1/2}$,Ta$_{1/2}$)O$_3$ and Ni$_3$B$_2$O$_{13}$I, but the search then declined, in large part because single-phase materials with both properties could not be widely produced and because of rather weak magnetoelectric coupling.

Why is it difficult to combine ferroelectricity and magnetism? In conventional ferroelectrics such as BaTiO$_3$, the transition ions (Ti in BaTiO$_3$) have empty $d$-shells.[3] The hybridization effects between these empty $d$ states and the filled oxygen $p$ states drives the off-centering of a cation ion towards the neighboring anion, inducing electric polarization. On the other hand, magnetism requires a partly filled $d$ shell. Thus the usual atomic-level mechanisms driving ferromagnetism and ferroelectricity are mutually exclusive, and multiferroics, in general, require a different mechanism of electric polarization than in prototypical ferroelectrics.

Recently, the combination of both theoretical breakthroughs, advances in the experimental methods of observing magnetic and electric domains, and the enormous development in the technique of preparing samples, have led to a renaissance in the field of magnetoelectric multiferroics.[4; 5; 6; 7] Several novel
ideas and concepts have emerged in understanding the coexistence of magnetic and electrical ordering and new classes of multiferroics have been discovered, such as (i) ferroelectricity induced by frustrated magnetism,[8; 9] (ii) non-centrosymmetric charge-ordering[10; 11], (iii) geometrical ferroelectricity,[12] and (iv) ferroelectricity induced by orbital ordering.[13] A substantial part of this thesis deals with materials that belong to the first class.

Magnetically driven multiferroics are insulating materials, mostly transition metal oxides, in which macroscopic electric polarization is induced by magnetic long-range order. The absence of inversion symmetry is a necessary (but not sufficient) condition for the appearance of spontaneous electric polarization. In these materials inversion symmetry, as well as time reversal symmetry is broken by magnetic ordering. Such a symmetry breaking often occurs in so-called frustrated magnets, where competing interactions between spins favor unconventional magnetic states. The microscopic mechanisms of magnetically-induced ferroelectricity involve the polarization of electronic orbitals and relative displacement of ions in response to magnetic ordering. These systems are classified as *improper* ferroelectrics since the primary order parameter is the magnetization, and ferroelectricity occurs as an accidental by-product. On the other hand, in conventional *proper* ferroelectrics, electric polarization is a primary order parameter describing the transition from the paraelectric to the ferroelectric phase.

Examples of magnetic ferroelectrics include the orthorombic rare-earth manganites $\text{RMnO}_3$ and $\text{RMn}_2\text{O}_5$ where $R$ denotes a rare earth ion. In $\text{TbMnO}_3$ and $\text{DyMnO}_3$ the onset of ferroelectricity is observably correlated to the appearance of spiral magnetic ordering. In these materials an applied magnetic field causes a spin flop transition, as a result of which the polarization vector rotates by $90^\circ$. The application of a magnetic field also enhances the dielectric constant (colossal magneto-dielectric effect) by as much as 500% in the case of $\text{DyMnO}_3$. Furthermore, a periodic oscillating magnetic field between 0 and 2 T, can change the polarization direction by $180^\circ$ in $\text{TbMn}_2\text{O}_5$, i.e. the polarization vector can be flipped by magnetic field. In applied magnetic field the dielectric constant increases by as much as 109% in the case of $\text{DyMn}_2\text{O}_5$.

The magnetoelectric interactions that induce electric polarization in magnets can also couple oscillations of magnetization to polar lattice vibrations, resulting in novel excitations called electromagnons. Electromagnons are spin waves that can be excited by an oscillating electric field of light. Although electromagnons were predicted nearly 40 years ago, they were first observed recently in two groups of multiferroic orthorombic manganites, $\text{RMnO}_3$ ($R = \text{Gd,Tb,Dy,Eu}_{1-x}\text{Y}_x$) and $\text{RMn}_2\text{O}_5$ ($R = \text{Y,Tb}$). In particular, far infrared
spectroscopy of TbMnO$_3$ revealed the presence of electric active modes at magnon frequencies, which exist only in the ferroelectric phase with incommensurate magnetic order. In an external field this incommensurate state is suppressed and the electromagnon peaks in the absorption are wiped out. A key issue discussed here concerns the mechanism that couples phonons to magnons.

An alternative mechanism of improper multiferroicity, which allows both large polarizations and strong magnetoelectric couplings, is ferroelectricity arising from specific charge configurations in charge ordering insulators. Several compounds have been proposed, with the best case having been made for LuFe$_2$O$_4$ with the polarization induced by charge ordering below 350K. Charge order occurs when transition metal ions with different valence form an ordered superlattice, for instance the checkerboard alternation of Mn$^{3+}$ and Mn$^{4+}$ ions in La$_{0.5}$Ca$_{0.5}$MnO$_3$. This type of charge ordered state is referred to as ‘site-centered’ charge ordering. However, there exists another type of charge ordering often observed in quasi-one-dimensional conductors namely the formation of a ‘bond-centered’ charge density wave. In the bond ordered state neighboring sites along the chain form pairs leaving behind a pattern of alternating strong and weak bonds. It has been suggested that the coexistence of bond- and site-centered orders can result in a non-centrosymmetric charge distribution and thus give rise to polarization. This mechanism is interesting in that it may be at work in half-doped manganites well-known for colossal magnetoresistance and electronic phase separation.

Magnetoelectrics and multiferroics are examples of the broader class of multifunctional materials that merge several useful features in the same substance and display new phenomena that are more than just the sum of the individual parts. For example, the coupling between ferroelectric and ferromagnetic properties gives rise to electric-field-switchable magnetization and vice versa. Such coupling could find its application in data-storage devices. In addition one could envisage that both magnetization and polarization could independently encode information in a single multiferroic bit. Although, technological applications take considerable time to be realized, the physics of these materials is full of surprises and is will undoubtedly give rise to challenging phenomena in the near future.
Outline of this thesis

In Chapter 2 basic principles of theory of magnetoelectric and multiferroic materials are examined. We first discuss a phenomenological approach to the magnetoelectric effect, and then turn to the microscopic mechanisms that give rise to ferroelectricity in frustrated magnets where competing interactions between spins result in states without inversion symmetry. This chapter is concluded with an introduction to dipole excitations of spin waves, or electromagnons which is a common theme in the Chapters 3-5.

In Chapter 3 we focus on the rare earth manganites with chemical formula $R\text{Mn}_2\text{O}_5$ ($R$ is a rare earth ion). We present a realistic microscopic model incorporating the structural characteristics of this family of manganites and calculate the spin-wave dispersion and the dynamical structure factor, which we compare to inelastic neutron scattering data on $\text{YMn}_2\text{O}_5$. We also discuss a mechanism of magnetoelectric coupling that only involves the isotropic Heisenberg exchange between non-collinear spins and show how this coupling gives rise to electromagnons in agreement with the sharp electromagnon peak observed in far-infrared optical absorption measurements.

In Chapter 4 we consider a model of the $R\text{MnO}_3$ multiferroics. Linear spin wave theory is used to calculate the dispersion relation of the one magnon excitations. The model calculations for the dynamical structure factor are compared with experimental results on $\text{TbMnO}_3$ and the origin of the electromagnon peaks in the non-collinear spin state is reviewed. Furthermore, we estimate the quantum corrections to the ground state sublattice magnetizations due to zero-point spin-wave fluctuations and show that the combined effect of single-ion anisotropy and quantum fluctuations gives rise to the elliptic spiral spin structures.

In Chapter 5 we show that strong electromagnon peaks can be found in absorption spectra of non-collinear magnets exhibiting a linear magnetoelectric effect. The frequencies of these peaks coincide with the frequencies of antiferromagnetic resonances and the ratio of the spectral weights of the electromagnon and antiferromagnetic resonance is related to the ratio of the static magneto-electric constant and magnetic susceptibility. Using a Kagomé lattice antiferromagnet as an example, we show that frustration of spin ordering gives rise to magnetoelastic instabilities at strong spin-lattice coupling, which transform a non-collinear magnetoelectric spin state into a collinear multiferroic state with a spontaneous electric polarization and magnetization. The Kagomé lattice antiferromagnet also shows a ferroelectric incommensurate-spiral phase, where polarization is induced by the exchange striction mechanism.

Magnetically tuneable electric polarization and giant magnetoelectric ef-
fects are not restricted to occur only in frustrated magnets. Electric polarization was also observed in materials with acentric charge and orbital orders. It was recently predicted that the interplay between charge, orbital, and spin degrees of freedom in doped manganites results in coexistence of site-centered and bond-centered charge orders, which breaks inversion and makes these materials ferroelectric. In Chapter 6 we study the coexistence of two different charge orders within phenomenological Landau theory and show that the resulting ferroelectric states are unstable against an incommensurate modulation of the electron density. This instability breaks the homogeneous states into ferroelectric domains separated by electrically charged domain walls. As temperature decreases and the amplitude of the charge modulation grows, the ferroelectric phase may become stable, but it still may contain a single domain wall with a negative free energy.

Finally, in Chapter 7 we study the role of kinks in a quasi one-dimensional frustrated (spin-)Peierls system and show that interchain coupling and lattice fluctuations can give rise to instability of the uniform dimerized Peierls state and stabilize in a finite temperature interval a periodic soliton lattice. The results are compared with the properties of the spin-Peierls compounds TiOCl and TiOBr that exhibit an zero field incommensurate phase intervening between the uniform spin-Peierls phase and the paramagnetic phase.
Bibliography
